



Role of cellulose fibers in enhancing photosensitized oxidation of basic green 1 with massive dyeing auxiliaries

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ABSTRACT

Due to their abundance, high natural affinity to various reactants, cellulose fibers (CFs) are promising catalyst supports for real wastewater treatment. Herein, a new visible-light-responsive cellulose fibers-supported zinc tetra(2,4-dichloro-1,3,5-triazine)aminophthalocyanine (denoted as Zn-TDTAPc-F) catalyst system was fabricated for removing dyes from aqueous solution in the presence of massive dyeing auxiliaries. In contrast to most traditional radical-dominated catalytic systems in which dyeing auxiliaries always play negative roles, the photosensitized oxidation of BG1 over Zn-TDTAPc-F catalyst has been obviously enhanced with auxiliaries such as NaCl, urea and isopropanol, most likely owing to the “primitive” outstanding properties of CFs such as their controllable surface charge (zeta potential), good swelling properties and intermolecular hydrogen bonding structures as well as the participation of non-radical singlet oxygen as the primary oxidant. On the basis of our experimental observations, a possible photosensitized oxidation mechanism including the photogeneration of singlet oxygen and the fundamental roles of CFs have been discussed in detail. These findings provide a new approach for removing highly hazardous target pollutants in actual wastewater with massive organic and inorganic substances, and further set a good example for the design and optimization of the catalyst via well controlling the supports.

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1. Introduction

Catalyst support technology has been proved as an effective approach to improve the catalytic activity, dispersion and stability of the supported catalysts [1,2]. However, the future growth of the catalysis will depend on the better understanding and subsequent control of the chemistry of catalyst supports (and not only on the surface area and porosity, as it was the conventional case for inorganic catalyst supports), which can then be exploited in the design of truly unique catalysts. Cellulose is an organic compound consisting of a linear chain of several hundred to over ten thousand $\beta(1 \rightarrow 4)$ linked D-glucose units. As a common cellulose derivative, cellulose fiber (CF) is identified as an almost inexhaustible source of chemical raw material as it is the most abundant organic polymer on earth [3–6]. Due to their inherently outstanding properties of hydrophilicity, chirality and broad chemical variability, CFs have showed fascinating potentials as environmentally friendly and biocompatible supports for a range of catalysts [7,8]. Previously, we have reported that cobalt phthalocyanine supported on CFs enabled

a dramatic improvement of catalytic efficiency in a H_2O_2 -involved dye degradation system, where CFs served as unique phase-transfer mediums [9], but very few studies have addressed the role of CFs in catalytic processes.

From a viewpoint of environmental protection, the elimination of highly toxic and recalcitrant persistent organic pollutants (POPs, such as conjugated dyes, chlorinated aromatic compounds, polybrominated diphenyl ethers, endocrine disrupting chemicals, antibiotics) at a relatively low concentration has become the concern of the international frontier research [10,11]. Among them, real dye wastewater is rather difficult to deal with because of its heavy chroma, chemically inert structure and complex components [12–14]. Different kinds of organic/inorganic dyeing auxiliaries (e.g., salts, alcohols, and urea) are artificially added during the dyeing process to facilitate the effective penetration of dyes into fabrics, such that a large mass of auxiliaries (typically at least 100–1000 times higher than the residual dyes) will still leave in the wastewater. These auxiliaries are usually detrimental to certain catalytic systems where reactive oxygen species (ROS) dominate the redox process since some auxiliaries are more inclined to recombine with the ROS (e.g., $\cdot OH$ radical) than that of targeted organic dyes [15–18]. For these reasons, currently there are few effective and inexpensive technologies for removing residue dyes from wastewater in the presence of massive auxiliaries [19–21].

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In this respect, a visible-light-initiated, radical-free and molecular oxygen-participated catalytic system seems to be extraordinarily attractive for practical treatment of real dye wastewater. Zinc phthalocyanine (ZnPc) is such a promising candidate catalyst. Specifically, ZnPc is a special photosensitizer that can be excited in a wide visible spectrum (600–800 nm) [22–25], and more importantly, it is able to photochemically activate triplet oxygen into singlet oxygen ($^1\text{O}_2$), a powerful non-radical oxidant that has been frequently used for decomposing stable organics.

In this work, hybrid CFs supported ZnPc photocatalysts (Zn-TDTAPc-F) were prepared by a covalent grafting method. The visible-light photoactivity of Zn-TDTAPc-F toward aqueous basic green 1 (BG1) degradation with/without the addition of auxiliaries has been investigated, where oxygen was employed as the primary oxidant to generate $^1\text{O}_2$ species. The positive effects of typical additives (i.e., NaCl, urea, and isopropanol) with a wide concentration range on the photosensitized oxidation of BG1 are systematically examined, which provides a full understanding of the physical/chemical interactions between CFs and auxiliaries in enhancing the photoactivity. Finally, based on our experimental observations, a possible reaction mechanism has been proposed to elucidate the roles of CFs during photosensitized oxidation of aqueous BG1 into non-hazardous small products.

2. Experimental

2.1. Materials

CFs were obtained from Fulida Co., Ltd. (China). BG1 and cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Zinc chloride hexahydrate, ammonium molybdate, urea, NaCl, isopropanol and benzene were analytical reagents and used without further purification.

2.2. Preparation of Zn-TDTAPc-F

Zinc tetraaminophthalocyanine (ZnAPc) was prepared according to previous methods [9], and Zn-TDTAPc-F was prepared by immobilizing zinc tetra(2,4-dichloro-1,3,5-triazine)aminophthalocyanine (Zn-TDTAPc) on CFs with covalent bonds. To compare the catalytic activity of Zn-TDTAPc-F with homogeneous phthalocyanine, zinc tetra(N-carboxylacrylic)aminophthalocyanine (ZnMPc) was prepared according to previous study [26]. The chemical structures of ZnPc derivatives, the preparation process of Zn-TDTAPc and CFs supported ZnPc are illustrated in Scheme SM-1.

2.3. Photosensitized oxidation of BG1

The photosensitized oxidation of BG1 was carried out in a 40 mL glass sample beaker at ambient temperature and atmospheric pressure with side irradiation provided by a 100W lamp (LOT-orient GmbH & Co. KG). A UV cutoff filter (Shanghai Seagull Colored Optical Glass Co., Ltd.) was employed to supply visible light with $\lambda > 400$ nm. Initial concentrations or amount of a typical reaction mixture were controlled as follows: (a) dye BG1 (50 μM , 10 mL); (b) Zn-TDTAPc-F (0.05 g, containing 0.208 μmol ZnPc, determined by atomic absorption spectrometry, Thermo Sollar M6). The contrast experiment of homogeneous catalysis maintained the molar concentration of ZnMPc equal to ZnPc in Zn-TDTAPc-F. At given time intervals, UV-visible spectrometer (U-3010 spectrophotometer, HITACHI) was employed to analyze the samples immediately at the corresponding maximum absorbance of the dye. To ensure the credibility of the research results, the same experiment was

conducted for four times. The photosensitized oxidation efficiency is characterized by residual rate:

$$\text{Residual rate (\%)} = \frac{C}{C_0} \times 100 = \frac{A}{A_0} \times 100$$

where C_0 , C , A_0 and A represent the initial concentration of dye, the concentration of dye after irradiation in selected time interval, the initial absorbance value, and variable absorbance value, respectively. Unless explicitly stated, the experiments were all carried out in neutral solutions. The pH of BG1 solutions was adjusted by 0.1 M HCl or 0.1 M NaOH.

2.4. Characterization

Biological microscope (Olympus 1X71) was used to observe the cross-sections of CFs. Scanning electron microscopy (SEM) images of the cross-sections of Zn-TDTAPc-F with or without treating by urea (125 mM) were taken by a JSM-5610V scanning electron microscope (TEOL, Japan).

2.5. Determination of the zeta potential of fibers

Electro kinetic surface properties of materials are generated by the electrochemical double layer [27], existing at the phase boundaries between the surface and electrolyte solutions. Here the streaming potential method [28] was used to study the zeta potential of cellulosic systems. The detection method of zeta potential (ζ) was described specifically in supplementary material. The zeta potential of CFs was measured by the Surpass electro kinetic analyzer (Anton Paar GmbH). The streaming potential was measured as a function of electrolyte concentration in neutral, concentrations of NaCl electrolyte ranged from 10^{-4} to 10^2 mM, and the surface conductivity was not taken into account.

2.6. Swelling measurement

To investigate the interaction between auxiliaries and CFs, the swelling ratio (SR) measurement of Zn-TDTAPc-F in aqueous solutions with or without auxiliaries were carried out by benzene retention according to the literature method [29] at room temperature and 60% relative humidity. The oven-dried fibers (0.3 g per serving) were immersed in different concentrations of auxiliaries solutions (0, 5, 25, 75, 125 mM urea/isopropanol and 0, 25, 50, 75, 125, 250 mM NaCl, respectively) at room temperature for one day until reaching swelling equilibrium before testing. The apparatus used for measurement of cellulosic swelling ratios is a 5 mL pycnometer and a sensitive balance. The test principle and calculation formula of SR value were listed in supplementary material.

2.7. Mechanism and intermediates analysis

EPR (Bruker A300), UPLC-HDMS (Waters UPLC Synapt G2-S HDMS) and GC-MS (Agilent 6890N) were utilized to detect possible intermediates formed in the reaction system. The testing conditions are listed in supplementary material.

3. Results and discussion

3.1. Photosensitized oxidation of BG1

First of all, the adsorption behavior and photosensitized oxidation of BG1 using Zn-TDTAPc-F catalysts were initially carried out under various experimental conditions for four times. As shown in Fig. 1a, it is noted that more than 98% of BG1 has been destroyed after visible light irradiation for 90 min (black line), demonstrating the promising visible photosensitized property of Zn-TDTAPc-F. In

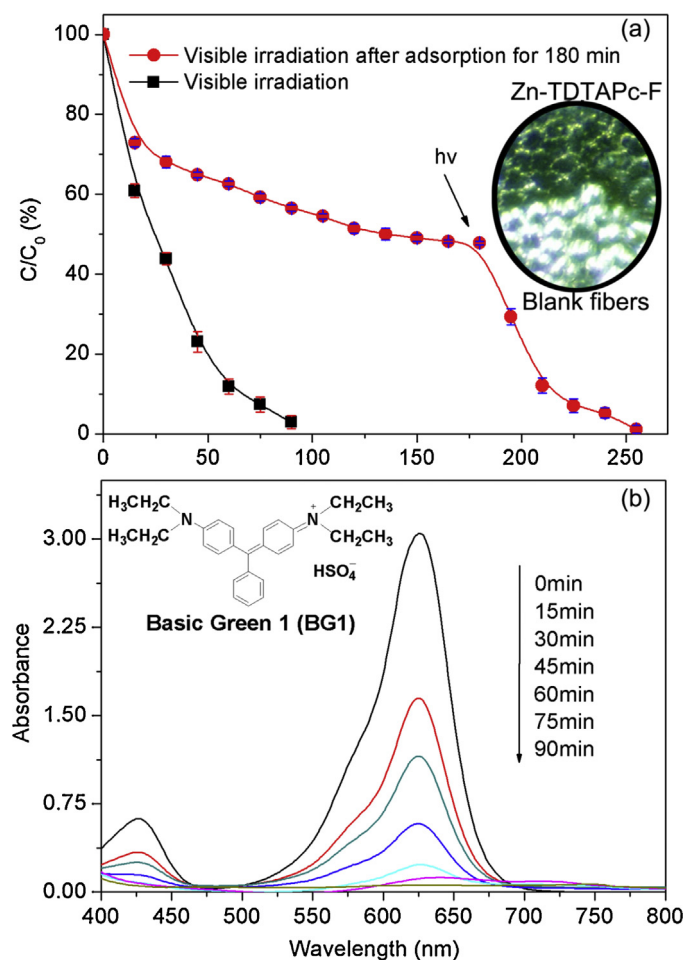


Fig. 1. (a) The plot of relative concentration (C/C_0) versus irradiation time for the adsorption and photosensitized oxidation of BG1 using Zn-TDTAPc-F with or without visible irradiation (monitored at 624 nm). (b) Time dependent UV–vis spectral changes of BG1 in the presence of Zn-TDTAPc-F under visible irradiation, 25 °C, pH 7. Inset: the photo-micrographs of cross sections of Zn-TDTAPc-F (top) in green color and blank cellulose fibers (bottom) in white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

contrast, under dark conditions, less than 50% of BG1 was gradually adsorbed onto Zn-TDTAPc-F and reached adsorption–desorption equilibrium within 180 min. As soon as visible light was onset, the concentration of BG1 was reduced rapidly in subsequent 30 min, and almost all of BG1 dyes were removed after visible irradiation for 90 min (red line). The corresponding significant decline at the maximum absorption peak of BG1 (624 nm) upon continuous visible light irradiation was clearly observed according to the time dependent UV–vis spectra (Fig. 1b), indicating that the chromophores structure of BG1 has been completely destroyed within 90 min photoreaction. In addition, no obvious dye peak decrease was observed in the bare BG1 aqueous solution under visible irradiation (curve a, Fig. SM-1), suggesting that the photolysis of dyes could be neglected. Importantly, if N_2 instead of O_2 was bubbled into the reaction system to reduce the O_2 content, no significant difference in the adsorption of BG1 by Zn-TDTAPc-F was found (curve c and curve d, Fig. SM-1), but the degradation degree of BG1 was greatly weakened to a value of only 40% (curve e and curve f, Fig. SM-1), indicating that O_2 serves as the main oxidant in the present photoreaction system.

When homogeneous ZnMPc catalyst was used for the same photosensitized oxidation, the removal rate of BG1 was prohibited to be more than 30% than that of Zn-TDTAPc-F catalyst (Fig. SM-2), such that the catalytic activity of ZnPc has been indeed enhanced by

introducing CFs as the catalyst support. As compared with blank CFs in white, the photo-micrographs of cross sections of Zn-TDTAPc-F exhibits green color throughout the surface and interspaces of CFs (inset in Fig. 1a), demonstrating that the ZnPc sensitizer has been successfully supported on CFs. As a consequence, the photosensitized oxidation process can not only occur on the surfaces but also within the bulk space of CFs. Due to the excellent adsorption affinity between cellulosic support and dyes, the fiber support is able to reduce the serious stacking and aggregation problems of homogeneous ZnPc for an efficient use of photosensitizer. Moreover, the fiber matrix is likely to play an important role in stimulating the photosensitized oxidation process mainly by concentrating dyes and catalytically active sites, and thus providing a proper microenvironment for a prompt catalytic reaction, as also described in our previous study.

3.2. Photosensitized oxidation with various auxiliaries

As mentioned above, dye wastewater always contains massive auxiliaries such as inorganic salts, detergents, solvents and other compounds, which are detrimental to some conventional wastewater treatment processes, thus the effects of auxiliaries on the photosensitized oxidation of dyes should be taken into consideration from the viewpoint of practical wastewater treatment. As common additives in dye wastewater [30–33], in this work, NaCl, urea and alcohols were selected as three typical auxiliary compounds.

3.2.1. Photosensitized oxidation with NaCl

NaCl has been widely used in textile dyeing process [34], because it can drive dye molecules into the interface and interior of CFs by changing the surface potential of fibers [35,36] and/or by reducing the solubility of dyes in aqueous phase [37], which we call potential effect and salting-out effect, respectively. Through these two effects, the introduction of NaCl with concentration ranging from 0 to 250 mM has largely changed the adsorption behavior as well as photosensitized oxidation of BG1 over Zn-TDTAPc-F (Fig. SM-3). As shown in Fig. 2b, the original surface of Zn-TDTAPc-F at pH 7 is negatively charged and the absolute value of zeta potential (ζ_{abs}) reaches maximum when the NaCl concentration increased from 0 to 75 mM. There are sufficient counter ions to form the electrical double layer near the Zn-TDTAPc-F surface with the increasing of ionic strength in solution [38,39]. Therefore, at low NaCl concentrations below 75 mM, the adsorption rate is determined by the potential effect. However, since the inner cationic layer has already been preferentially adsorbed onto the fiber surface, the adsorption rate of cationic dye decreased due to the electrostatic repulsion [40], leading to the slightly hold-up of BG1 adsorption in first 15 min (Fig. 2a). On the other hand, the ζ_{abs} decreased gradually with the NaCl concentration increasing to higher than 75 mM, resulting in the great reduction of negative charges on the Zn-TDTAPc-F surface. Theoretically, the adsorption rate of BG1 on Zn-TDTAPc-F should be reduced, but apparent improvement of adsorption was observed. This may be caused by the decisive salting-out effect, the dyes are more likely to be “pushed out” from the aqueous solution by inorganic salts into CFs, which exhibit a higher affinity to dye molecules.

Interestingly, even though the adsorption of BG1 was inhibited by NaCl at lower concentration, the photosensitized oxidation of BG1 by Zn-TDTAPc-F was still improved by the addition of NaCl in this concentration range. We believed that the inhibition of NaCl on BG1 adsorption just occurred on the surface of CFs and a fast release of reaction products resulted in much easier access for BG1 molecules to arrive at the interior active sites of Zn-TDTAPc-F, and followed by the rapid oxidation of BG1. On the other side, the enhanced adsorption of BG1 at higher NaCl concentration above

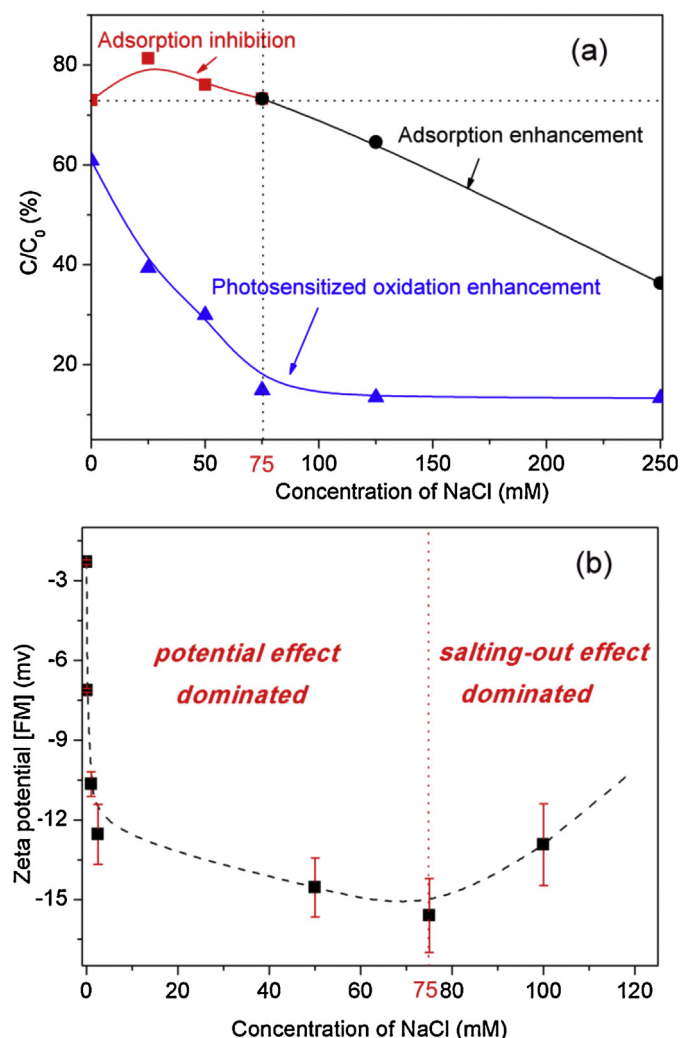


Fig. 2. (a) The effect of added NaCl concentration on adsorption and photosensitized oxidation of BG1 by Zn-TDTAPc-F after reaction for 15 min. (b) The effect of added NaCl concentration on zeta potential of Zn-TDTAPc-F at pH 7.

75 mM significantly improved the photosensitized oxidation process. Consequently, the controllable surface charge of CFs allows them to significantly improve the photosensitized oxidation of organic pollutants in the presence of salt auxiliaries.

3.2.2. Photosensitized oxidation with Urea

Since urea is easy to permeate into fibers [41] and is advantageous to the dye pickup, it is used as a common auxiliary in the textile printing and dyeing industry. With the addition of urea, the adsorption and the photosensitized oxidation of BG1 by Zn-TDTAPc-F were both improved in the initial 15 min photoreaction (Fig. 3a), and BG1 was completely removed within 30 min under visible irradiation (Fig. SM-4), suggesting that the oxidative degradation of BG1 was greatly enhanced in the presence of urea. In this case, it is supposed that the swelling effects of urea on the CFs may be attributable to the improved photo oxidation efficiency. According to the swelling measurement, the fabrics swelling ratios obtained in urea solutions were apparently higher than that in distilled water, and they increased with the urea concentrations increasing (Fig. 3b). Moreover, the cross-section areas of single Zn-TDTAPc-F (ASF) were apparently enlarged after the swelling process according to SEM analysis (Fig. 4). Since urea can break the intermolecular bonds in cellulose fibers by the produced internal stresses [42,43], the regularity of cellulose molecular chains will

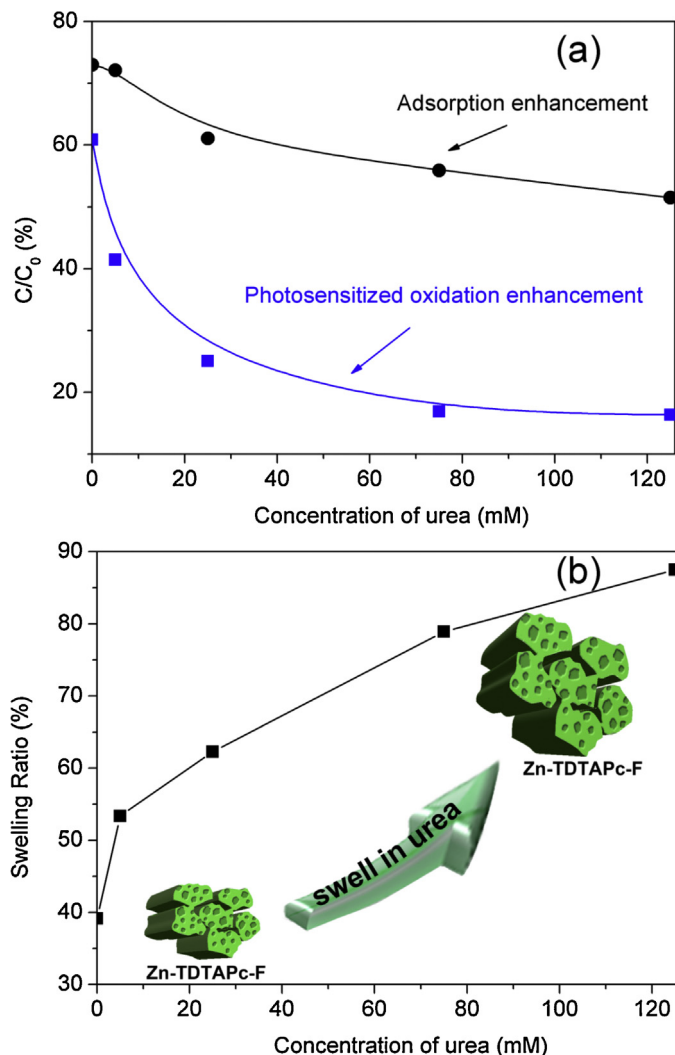


Fig. 3. (a) The effect of urea concentration on adsorption and photosensitized oxidation of BG1 by Zn-TDTAPc-F after reaction for 15 min. (b) The effect of urea concentration on swelling ratio of Zn-TDTAPc-F and conceptual representation of the cellulose swelling process in urea, 25 °C, pH 7.

be reduced and the surface area will be increased after urea permeation, leading to the convenient approaching of dye molecules to the reactive sites. Therefore, owing to their excellent swelling performance in urea, CFs are able to significantly improve the adsorption and photosensitized oxidation of organic pollutants.

3.2.3. Photosensitized oxidation with isopropanol

In addition to NaCl and urea, the textile wastewater also contains numerous hydroxyl group-containing compounds, such as PVA [33] and PEG serving as sizing agents in textile finishing and hydrophilic groups of popular non-ionic surfactants, respectively. Herein, isopropanol, a widely used efficient radical scavenger [17], was employed to investigate the effect of hydroxyl group-containing compounds on this photosensitized oxidation system. As shown in Fig. 5a and Fig. SM-5, similar to NaCl and urea, in the presence of isopropanol solutions ranging from 5 to 125 mM, both the adsorption and photosensitized oxidation of BG1 were enhanced, and nearly all of BG1 were removed within 30 min. Because of the surface compatibility [44] between CFs and hydroxyl group-containing compounds, these compounds are suggested to easily permeate into the interspaces of fibers not only by increasing the swelling ratio (which was increased by almost 10%, Fig. SM-6), but also by replacing the water interspaces within CFs. As a result,

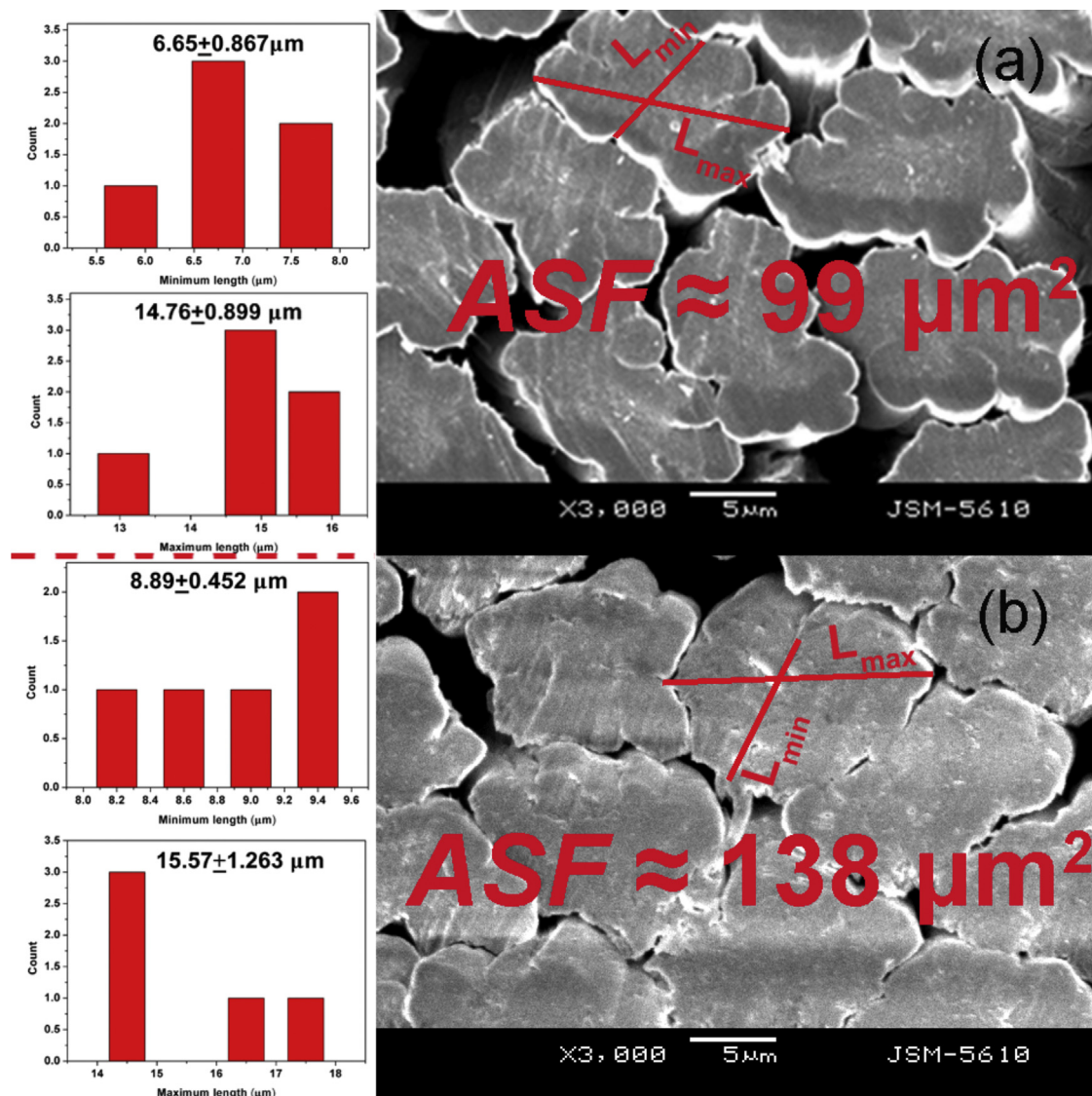


Fig. 4. The SEM images of Zn-TDTAPc-F cross-sections dealt with or without urea (125 mM) and their statistical distribution, 25 °C, pH 7. (a) Dealt in water and (b) dealt in urea solution.

the alkyl-chain contained dye molecules, which preferred to be dissolved in alcohol, were promptly moved forward into the inter-spaces of amorphous region in CFs [45] where dye molecules have been swallowed. The graphical representation of the cellulose permeation by the dye solution containing hydroxyl group-containing compounds is illustrated in Fig. 5b, which leads to the enhanced photoactivity of Zn-TDTAPc-F toward BG1 degradation.

3.2.4. Photosensitized oxidation with various auxiliaries

To further explore the activity of Zn-TDTAPc-F with various auxiliaries, the adsorption and photosensitized oxidation of BG1 in the coexistence of 25 mM NaCl, urea and isopropanol respectively were conducted. As shown in Fig. 6, both the two processes were improved, and all of BG1 dyes were removed within 45 min, which is much faster than the system without auxiliaries. Accordingly, the utilization of CFs with understanding properties like controllable surface charge, good swelling properties and inter-molecular hydrogen bonding structures has obviously led to the preferential photooxidation of dye molecules in the presence of massive organic/inorganic compounds. In contrast to most AOPs (like Fenton and Fenton-like systems) [46,47], the presence of radical scavengers (Cl^- and isopropanol) has negligible effect on the

photosensitized oxidation of BG1, indicating that normal radicals like hydroxyl radicals and superoxide radicals [48] are not the dominant ROS involved in this photooxidation process.

3.3. Effect of pH and regeneration performance

Fig. SM-7 shows the adsorption and photosensitized oxidation of BG1 using Zn-TDTAPc-F at pH 3, 7 and 10. No significant difference on the adsorption of BG1 at different pH values was observed. In alkaline condition, considering the accumulation of negative charges on CFs, the adsorption of cationic BG1 molecules should have been increased, but no obviously promotion of adsorption was found. This may be attributed to the effect of pH on the restructuring of BG1 because the dye molecules tend to combine with hydroxyl with the increase of alkalinity (Fig. SM-8) [49,50]. On the other hand, Zn-TDTAPc-F exhibits a higher photosensitized oxidative activity at neutral or alkaline pH than that in acidic solution, which is supposed to be caused by the relatively poor planar conjugation of BG1 at higher pH (see the detailed analysis in Supplementary Material). The above results were rather different from traditional Fenton and Fenton-like systems in which the catalysts have much higher catalytic activity in acidic solution than alkaline.

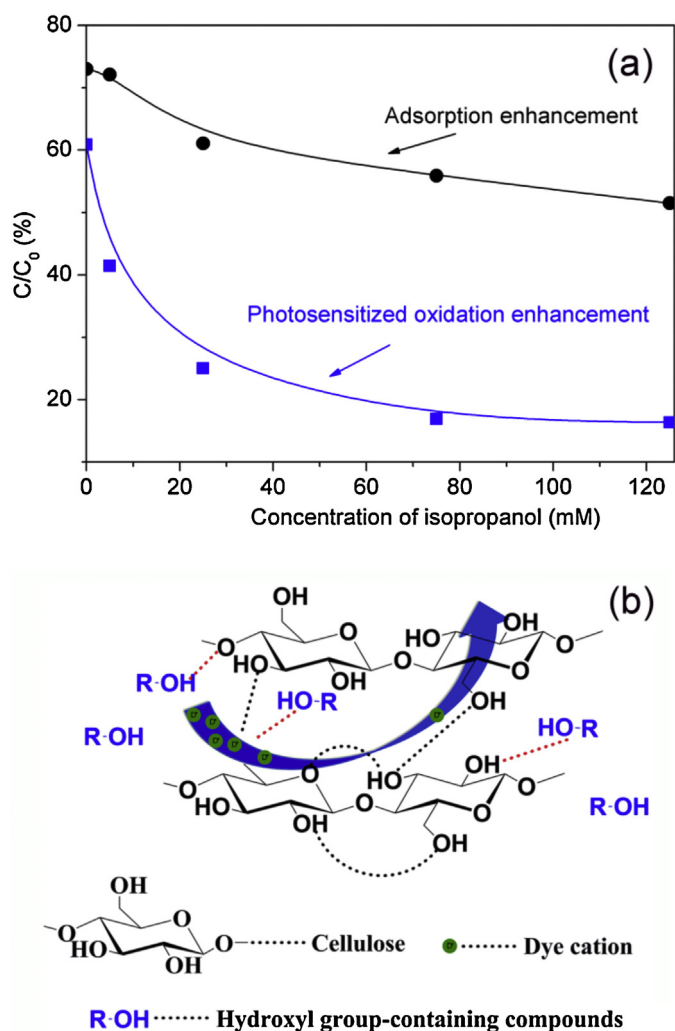


Fig. 5. (a) The effect of isopropanol concentration on adsorption and photosensitized oxidation of BG1 by Zn-TDTAPc-F after reaction for 15 min, 25°C, pH 7. (b) Conceptual representation of the dye permeation into cellulose in the presence of hydroxyl group-containing compounds.

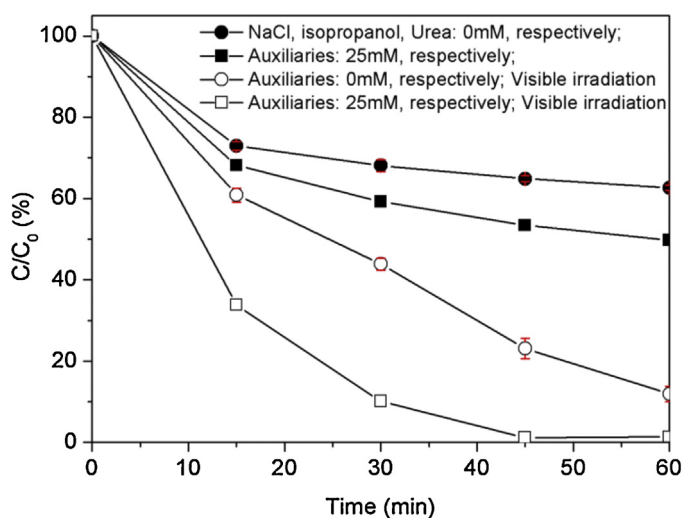


Fig. 6. Adsorption and photosensitized oxidation of BG1 by Zn-TDTAPc-F in presence of the mixture of NaCl, urea and isopropanol.

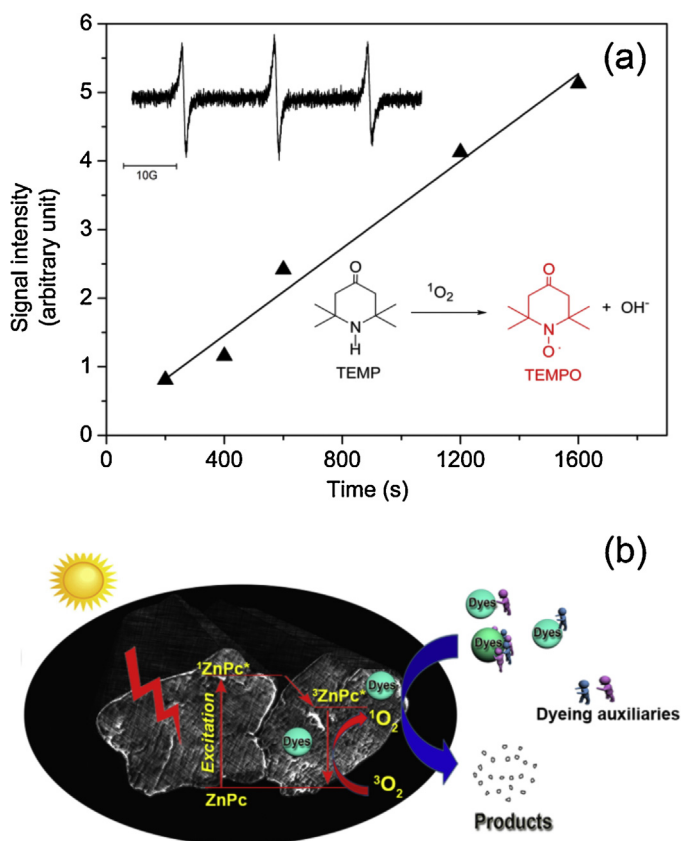


Fig. 7. (a) Irradiation time dependence of the EPR signal intensity of TEMP- 1O_2 adduct in oxygen-saturated BG1 aqueous solution with Zn-TDTAPc-F. (b) The proposed mechanism of the photosensitized oxidation of BG1 by Zn-TDTAPc-F in the presence of auxiliaries.

It is worth noting that real dye wastewater is always in neutral and alkaline conditions [51], such that the present photosensitized oxidative system is potentially applicable for practical wastewater treatment.

Moreover, the regenerating performance is a key character of catalysts that to be usable in practice, thus the recycling experiments of Zn-TDTAPc-F were carried out. As shown in Fig. SM-10, after 4 runs of photosensitized oxidation, more than 90% of BG1 can still be removed, indicating that Zn-TDTAPc-F possesses relatively good regeneration ability. The slight decline in activity after four cycles might be due to the loss of shattered fibers during the process of sampling.

3.4. Mechanism and pathway

3.4.1. Mechanism

The elucidation of reaction mechanism is important to further fabricate catalysts with enhanced catalytic properties. Consequently, EPR spin-trapping technique was employed to investigate the current reaction mechanism. Using TEMP as the spin-trapping agent [52,53], a triplet lines corresponding to TEMP adduct was obtained (inset of Fig. 7a). Since TEMP can be oxidized to a stable N-oxyl radical (2,2,6,6-tetramethylpiperidine N-oxyl, TEMPO) under the attack of 1O_2 , the generation of 1O_2 could be confirmed. The plot of TEMP intensity vs. reaction time is presented in Fig. 7a. It is seen that the TEMP intensity increased with prolonging the reaction time, indicating that more and more 1O_2 species are generated upon continuous visible light irradiation. Additionally, DMPO spin-trapping EPR analysis of BG1 aqueous or methanol solutions shows that no hydroxyl radicals or peroxy radicals were

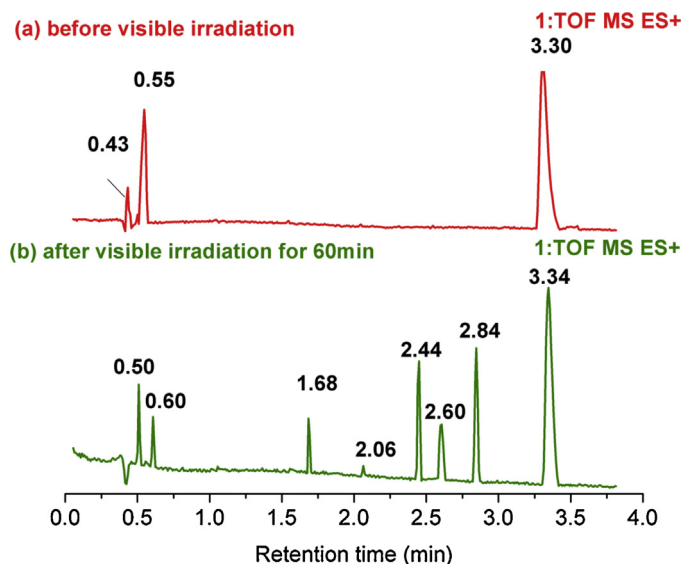


Fig. 8. The corresponding UPLC spectra profiles of the original BG1 solution and BG1 solution after visible irradiation for 60 min. Y-axis is partly enlarged because of the small amount of several intermediates.

generated during the photosensitized oxidation (Fig. SM-11). Therefore, the current photosensitized oxidation of BG1 using Zn-TDTAPc-F is indeed dominated by $^1\text{O}_2$ rather than other ROS, which is consistent with the aforementioned description. The generation of $^1\text{O}_2$ might follow the mechanism stated below: the excited triplet state of $^3\text{ZnPc}^*$ originated from visible irradiation and intersystem crossing mechanism interacts with ground state triplet oxygen ($^3\text{O}_2$) to the regeneration of ZnPc as well as the formation of highly active $^1\text{O}_2$ species [54,55], which participate in the successive oxidation of BG1 dyes (Fig. 7b). It can be concluded that Zn-TDTAPc-F has achieved the highly efficient removal of dyes at a relatively low concentration from wastewater with massive auxiliaries. Due to their controllable surface charge, good swelling property and intermolecular hydrogen bonding structure, CFs was proved to play extremely important roles in concentrating dyes and catalytic active sites, finally facilitating the rapid oxidation of dyes.

3.4.2. MS Determination

Process of the photosensitized oxidation of BG1 with Zn-TDTAPc-F was further confirmed by UPLC Synapt G2-S HDMS. After visible irradiation for 60 min, the maternal compound (BG1, $m/z = 385.2639$) and 10 compounds (P_1 – P_{10}) were identified as the possible intermediates during the photosensitized oxidation (Table SM-1, Table SM-2). Four intermediates (P_1 , P_5 , P_6 , P_8) were evidently observed, corresponding to peaks at 2.60, 2.44, 2.84 and 2.06 respectively in UPLC spectra (other species were not obvious due to their low contents) (Fig. 8). The possible reaction pathways can be deduced by analyzing the intermediates and products (several results of HDMS are shown in Fig. SM-12). The formations of intermediates P_1 , P_2 were determined in the reaction mixtures, which result from the *N*-deethylation of BG1 [56]. P_3 , P_4 formed from the hydrolysis and dehydroxylation of P_2 , while the generation of intermediates P_5 – P_{10} was due to the cleavage at the central carbon according to literatures [57,58] (based on dyes with similar chemical structures to BG1), and P_7 – P_9 generated from further *N*-deethylation of P_5 and P_6 . These variations indicated that the *N*-deethylation and cleavage of BG1 were stepwise processes.

Nine main residual organic acids and alcohol after the photosensitized oxidation of BG1 for 90 min have been identified (P_{11} – P_{19} in Table SM-3) using GC–MS. The origin GC–MS dates of intermediates (P_{11} – P_{19}) can be seen in Table SM-4. These organic products are

similar to the other photosensitized oxidation of dyes reported in literatures [59,60], which means that BG1 has not only lost *N*-ethyl groups but also suffered deep oxidation during the photosensitized oxidation by Zn-TDTAPc-F.

Based on previous reports [61,62] and above results, we tentatively proposed the pathway for the visible light induced photosensitized oxidation of BG1 by Zn-TDTAPc-F (Fig. SM-14). First of all, it is evident that $^1\text{O}_2$ is the dominating active species for bond breaking and loop open in the overall oxidation process (Fig. SM-13). In principle, $^1\text{O}_2$ could mainly attack the central carbon of BG1 and thus directly decolorize the dyes. The formation of four *N*-deethyl products (P_1 – P_4) and the disappearance of *N*-ethyls indicate that nitrogen centered radical may be formed during the destruction process. As illustrated in Table SM-1, a large amount of *N*-deethylated and cleavage intermediates (P_1 , P_5 , P_6 and P_8) were generated, thus we supposed that the *N*-deethylation and cleavage pathways occurred simultaneously. As the reaction proceeded, the deethylation process kept continuing, while the intermediates with two benzene rings (P_5 – P_9) were cleaved into a series of primary aromatic derivatives such as *p*-hydroxybenzoic acid, benzoic acid and phenol that were eventually oxidized into nonhazardous small molecules such as adipic acid, maleic acid, malic acid, oxalic acid, etc. To conclude the pathway, the combination of EPR, UPLC Synapt G2-S HDMS and GC–MS results showed that the photosensitized oxidation of BG1 by Zn-TDTAPc-F under visible irradiation mainly involved two parallel processes, that is, *N*-deethylation and chromospheres structure cleavage under the attack of $^1\text{O}_2$. Importantly, the reaction intermediates were ultimately oxidized into biodegradable aliphatic acids and aliphatic alcohols.

4. Conclusion

In summary, we reported a new approach for removing dyes using Zn-TDTAPc-F catalyst in the presence of massive organic/inorganic substances (mimicking practical wastewater) under visible irradiation. The dyes are ultimately oxidized into biodegradable small molecules, and an obvious enhancement of the photosensitized oxidation is achieved by the addition of typical auxiliaries mainly due to the excellent performance of CFs supports, including their controllable zeta potential, fine swelling properties and intermolecular hydrogen bonding structures as well as the involvement of non-radical $^1\text{O}_2$ species as the oxidant. The inherent unique features allowed CFs to act as potential supports of photo sensitizers for removing dyes from wastewater containing various organic/inorganic compounds, which has potential advantages to the treatment of real textile wastewater. Future studies will be conducted to remove extremely hazardous low-concentration pollutants (e.g., halides, dioxin, and pesticide) using the similar fibers supported catalysts in the presence of massive organic/inorganic compounds. The present study not only presents a new method for removing highly hazardous pollutants from actual wastewater, but also sets an example for the design and optimization of catalysts based on the well controlling of their supports.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflict of interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.10.015>.

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